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Correspondence: Reply to 'Strongly-driven $Re + CO_2$ redox reaction at high-pressure and high-temperature'

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Santamaria-Perez *et al.*[1] attempt to reproduce our CO_2–SiO_2 solid solution[2]. In their study[1], mixtures of CO_2 and SiO_2 similar to those studied in our work[2] were indirectly laser heated up to 2,400 K and 50 GPa by using Re as an internal heater, and a CO_2–SiO_2 solid solution was not obtained. Instead, the only temperature quenched crystalline phases identified by X-ray diffraction were: known polymorphs of pure CO_2 and SiO_2, Re and ReO_2. In particular, the structure of ReO_2 was identified as being the β-ReO_2 (Pbcn), which is a well known phase of this oxide discovered many decades ago (ref. 9 in the letter). ReO_2 was then inferred to form from a high P–T, $Re + CO_2$ redox reaction. Moreover, it is shown that β-ReO_2 may provide a better fit to our XRD pattern than the cristobalite-like CO_2–SiO_2 solid solution. A shadow is then cast on the very existence of this solid solution.

In light of this study[1], we have reanalysed all our data, and realized that more complex chemical reactions may have occurred in our samples due to the extreme high temperatures: T > 4,000 K. To make the reaction between CO_2 and SiO_2 as efficient as possible, we understood that starting from confined CO_2 in a SiO_2 zeolite was not sufficient and then we planned and managed to heat the sample at conditions where both CO_2 and SiO_2 are fluid. The aim was to react them together starting from an ideal, hot, highly mobile mixture. For achieving very high temperatures, we insulated diamond using thick NaCl layers pelleted on it. Then, in principle, we carefully avoided laser heating the Re gasket. Nevertheless, we recognize that the laser spot may have hit the gasket at some point and/or the hot fluid sample may have drifted toward the gasket where spurious reactions with Re may have occurred. We have now reanalysed all our XRD patterns, including those at room pressure where potential volatile components (for example, CO_2) are absent making data interpretation as simple and clean as possible. Indeed, we confirm that the β-ReO_2 provides a better fit to the new phase than cristobalite. The lack of XRD Bragg peaks of stishovite in our samples, which was found in the letter by Santamaria-Perez, may be easily explained with liquid SiO_2 being temperature quenched in a glassy form. Our results thus do not prove the existence of a CO_2–SiO_2 solid solution and β-ReO_2 is indeed one of the materials synthesized in our experiment. Also, Raman data show that the chemistry was even more complex in our study. We now have an alternative explanation for the dominant Raman peak with five, fine-structure components[2]. This spectrum matches exactly that of crystalline Cl_2 (ref. 3), which clearly came from a partial dissociation of the NaCl insulating layers. Incidentally, we note that very recent studies show that simple salts, such as NaCl and KCl, may undergo major chemical changes upon laser heating at high pressures[4,5] (see also ref. 5 for an updated Raman spectrum of solid Cl_2). We recall, as noted in our original paper[2], that some microcrystalline/amorphous carbon was also formed in our laser-heated sample. In conclusion, we think that our revised data interpretation is consistent with the very complex chemistry that occurred in our study under extreme conditions, one potential chemical reaction path being CO_2 decomposed and, as a result, both Re from the gasket and NaCl were partially oxidized by the available free oxygen. Pure, molecular chlorine was then released after oxidization of NaCl. Decomposition of CO_2 and oxidation of Re and NaCl finally led to free carbon available to form graphite. We can resume this potential reaction as:

$$n\mathrm{Re} + 2m\mathrm{NaCl} + l\mathrm{CO_2} \rightarrow n\mathrm{ReO_2} + \mathrm{Na_{2m}O_h} + m\mathrm{Cl_2} + l\mathrm{C(graphite)},\ \text{with}\ h + 2n = 2l. \quad (1)$$

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Additional information

Competing financial interests: The authors declare no competing financial interests.

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